Crystallization of Polymers

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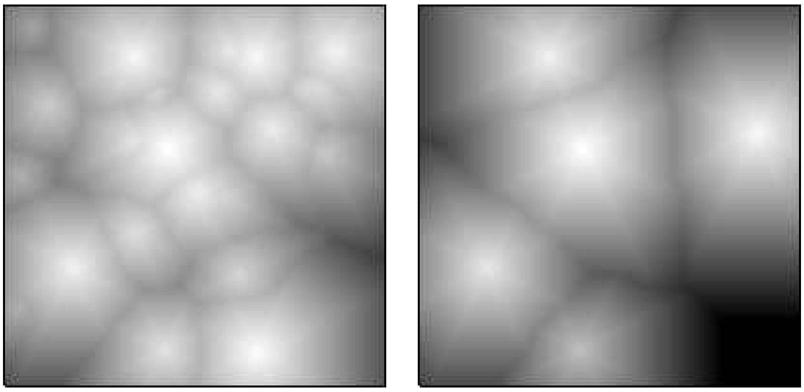
1 Introduction

Within the manufacturing industry there is a high demand for strong polymer base materials from which to make products. To produce a strong base material there are a number of possibilities, either: use a more expensive, denser polymer, or attempt to modify the mechanical properties of a cheaper, lighter polymer.

Polymers start life as high temperature liquids, which solidify as they cool. The cooling process has a large influence on the final *morphology* of the polymer (its internal crystalline structure). By controlling the cooling process it is possible to alter the morphology of the polymer and hence alter its mechanical properties (e.g., the fracture strength). When the polymer is composed of small, regular crystals (see figure 1(a)) it has a much higher fracture strength than when the polymer is composed of large, irregular crystals (see figure 1(b)).



(a) (b)

Figure 1: Two examples of different crystal morphologies. Panel (a) shows a finer morphology, while panel (b) shows a fairly coarse morphology.

The aim of this project is to simulate the cooling process and use the results from the simulations to optimise the cooling strategy and so produce polymers that have the desired morphology.

As the liquid polymer cools, it undergoes a phase change from liquid to solid. There are many possible ways to model this change of phase. The choice of model depends on the scales being considered. Possible models are:

(i) Micro-scale, considering the interactions of individual particles within the liquid polymer.

(ii) Meso-scale, considering the growth of individual crystals within the liquid polymer.

(iii) Macro-scale, considering the average state over the entire domain (e.g., 90% solid and 10% liquid).

Our goal is to determine an optimum cooling strategy to produce small regular crystals within the final solid. Hence we use a meso-scale model (ii); a micro-scale model (i) would also provide the necessary information, however the amount of computational effort required to use this model is excessive.

In section 2 we outline the modelling undertaken by Micheletti and Burger [MB01, Mic01]. We then describe the numerical issues encountered and the steps taken to solve them in section 3. Finally, we give some conclusions in section 4.

2 Modelling

The solidification of the liquid polymer is generally described by the following processes [MB01, Mic01]:

- As the temperature (having some distribution in the liquid) is decreased, nucleation points (the seeds of crystallization) are born. In general, the point of nucleation is to be considered as some random process in both time and space. Furthermore, the nucleation process is temperature dependent.
- From the nucleation points the actual crystal will start growing. The rate of growth is temperature dependent. As the crystallization takes place there is a release of latent heat along the crystal growth front. Consequently, there is a feedback loop between the nucleation and the crystal growth as both are dependent on the local temperature.
- As two crystal fronts meet in the liquid, the growth will terminate along the boundary thus resulting in the final morphology of the polymer.

Until the terminal state where all liquid has been solidified, the final morphology of the polymer is a matter of balance between the actual space occupied by crystals, birth of nucleation points, release of latent heat and the variation of the actual temperature field throughout the material.

Polymers are typically manufactured in large 3-dimensional vats. To simplify the numerical issues we consider throughout a single slice of the liquid polymer, reducing the problem to 2-dimensions.

2.1 Crystal nucleation

As we are not considering the details of the particle interactions within the liquid polymer we assume that the formation of nucleation points is a stochastic process. This is modelled as a Poisson process [CS00, Ede97, Dur99], where the stochastic intensity is the derivative of the crystal growth rate. The crystal growth rate is temperature dependent, consequently nucleation is a non-homogeneous Poisson process. The numerical results produced from this assumption closely match experimental data.

2.2 Crystal growth

Once a nucleation point is formed, a crystal begins to grow around it. When the temperature distribution is homogeneous throughout the polymer, the crystals formed are circular (or spherical when considering growth in $\mathbb{R}^3$).

Burger *et al.* [BCS02] use the *minimum-time principle* to extend the crystal growth to the case where the temperature distribution throughout the polymer is non-homogeneous. The minimum-time principle is "a crystal grows from its origin to any other point such that the needed time is minimal." Under the minimum-time principle, the growth of the crystal is shown to always be in a direction normal to the boundary of the crystal. The equations governing the growth of a particular crystal are

$$\begin{aligned} \dot{x}(t,\gamma) &= G(x(t,\gamma),t)n(t,\gamma), && \text{(1a)} \\ \dot{n}(t,\gamma) &= -\nabla G(x(t,\gamma),t) + \langle \nabla G(x(t,\gamma),t), n(t,\gamma)\rangle n(t,\gamma), && \text{(1b)} \end{aligned}$$

where n is the normalvector, γ is the parameterisation of the crystal boundary, and G is the growth rate of the crystal at a particular point in space and time. The polymer we consider in this report is isotactic polypropylene which has a growth function given by

$$G(x,t) = \begin{cases} aT(x,t) + b, & T(x,t) \geq 125, \\ cT^2(x,t) + dT(x,t) + e, & T(x,t) < 125, \end{cases} \tag{2}$$

where $a = -0.085825$, $b = 4.062614$, $c = -0.00133$, $d = 0.246637$, $e = -16.716251$ and $T(x,t)$ is the temperature at a particular location in time and space.

The equations (1) are insufficient to give the complete behaviour of the crystal growth as it does not include the effects of impacting crystals. Once two crystals collide the growth on the impinged region of the boundary ceases as there is no liquid polymer remaining to crystallise. In section 3.2 we discuss how we include the growth of multiple crystals into our simulation.

2.3 Temperature evolution

The evolution of the temperature distribution within the polymer can be modelled using the standard heat diffusion equation

$$\frac{\partial T}{\partial t} = c^2 \nabla^2 T. \tag{3}$$

The diffusion constant c is dependent on the phase of the polymer, i.e., as the polymer solidifies the value of c changes. However, in this report we assume that c remains fixed throughout space and time.

As the crystals grow, the solidification of polymer causes a production of latent heat at the boundary of the crystals. The injection of latent heat then affects the subsequent growth of the crystal and also the rate of nucleation. To include the effect of the latent heat we include a source term into equation (3) to give

$$\frac{\partial T}{\partial t} = c^2 \nabla^2 T + D \frac{\partial I_\Theta}{\partial t}. \tag{4}$$

where $\Theta \subset \mathbb{R}^2$ is the set of all points within the domain that are crystalline. The function I_Θ is an indicator function on this set that takes the value 0 or 1. The inclusion of the indicator function (specifically its derivative) means that (4) can only be interpreted in a weak sense. The stochasticity of Θ means that (4) is also a stochastic partial differential equation. The constant D is determined from the physical properties of the polymer considered.

3 Numerics

In this section we give details of the numerical approach taken to simulate the process of polymer crystallization.

Throughout the locations and sizes of the crystals present within the polymer are required. This information is necessary for three purposes: to ensure that new nucleation points are not created inside existing crystals, to restrict the growth of the crystals when they impact with each other, and to determine the amount of latent heat released into the polymer. To keep track of the crystals we use a *pixel matrix*. This is a discretization of the domain to a 400-by-400 matrix containing an integer value if there is crystal at a particular point, and 0 if there is not. The dimensions of this matrix are arbitrary, the values chosen here represent a good trade off between the computational speed and the accuracy of the final results. An example of the discretization used is illustrated in figure 2.

3.1 Crystal nucleation

As stated in section 2.1, the crystal nucleation is a non-homogeneous Poisson process with stochastic intensity $\lambda(x,t)$. We simulate this using the method outlined in [Dur99].

(i) Find $\lambda_{\max} := \max \lambda(x,t)$ over the entire domain.

(ii) Generate a random number with the Poisson distribution such that $n \sim \text{Poisson}(\lambda_{\max})$.

(iii) Generate n random points in space x_i, these are the potential nucleation points.

(iv) Using the pixel matrix, remove any points that occur inside already crystallized matter.

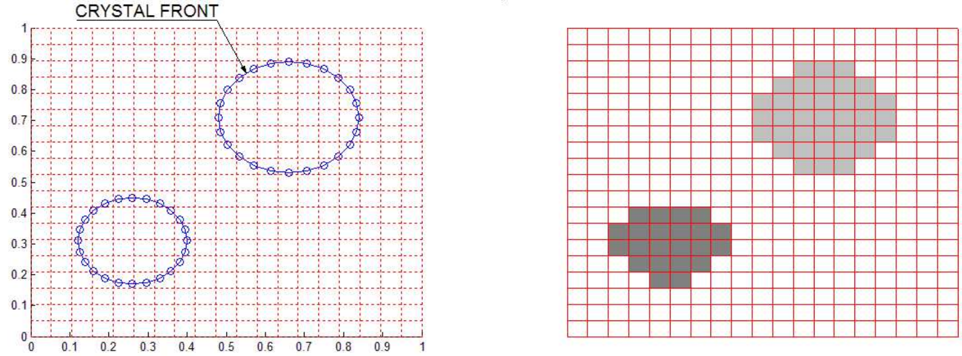
(v) For each potential nucleation point, generate a random number (uniformly distributed) and keep the point with probability $\lambda(x_i,t)/\lambda_{\max}$.

(vi) Update the pixel matrix with all the nucleation points retained.

These steps produce nucleation points that are Poisson distributed in space. However, as we step through time, this is only an approximation of a Poisson process in time.

3.2 Crystal growth

Next, we treat the actual growth of crystals, given some distribution of nucleation points. In the following it is important to note, that the growth can be handled separately i.e. in each time step we treat the crystals one-by-one in succession. Since the growth rate $G(x,t) = G(T(x,t)) = |n| = \frac{\mathrm{d}x}{\mathrm{d}t}$ is only temperature dependent it is fairly easy to calculate the evolution of the crystal front as $\mathrm{d}x = G(x,t)\mathrm{d}t$.



(a)

(b)

Figure 2: Panel (a): Discretization of spatial domain and crystal front. Panel (b): The corresponding pixel matrix. The spatial resolution depicted is rather coarse and therefore only instructional.

At this point it is suitable to introduce a discretization of the crystal front (see figure 2). Thus we only consider a limited (specifically, we used 25) number of points on the crystal front and letting these grow as dictated by (2). In order to be able to distinguish between solidified crystal and liquid, we construct a *pixel matrix*, P, of the same structure as the spacial discretization (i.e., 400-by-400) with entries

$$P(i,j) = \begin{cases} 0 & \text{if the point } x(i,j) \text{ is in liquid} \\ n(k) \in \mathbb{N} & \text{if the point } x(i,j) \text{ is in crystal no. } k. \end{cases}$$

The entry values $n(k) \in \mathbb{N},\ k \neq l \iff n(k) \neq n(l)$ are introduced in order to be able to distinguish between different crystals. Thus, as the crystals grow, their individual fronts will "sweep" over some points in the discretizised spatial grid (hence, resulting in changing zero-entries to $n(k)$ entries in P) - see figure 2. In this manner, we are able to determine the final tessellation simply by the resulting pixel matrix when all entries are nonzero. Note that P automatically take collision of crystal fronts into account.

In conclusion, the crystal growth is treated in the pseudo-code below. N denotes the total number of nucleation's points at time t.

```
for $i = 1$ to $N$
    - Check actual temperature distribution
    - Determine nucleation points in liquid
    - Calculate growth of crystals separately
    - Update zero elements of pixel matrix according to growth
end
```

Table 1: Pseudo-code for treating growth of crystals.

3.3 Temperature evolution

Equation (4) governs the temperature evolution within the polymer. As this is simply the standard heat equation with a source term, we can use standard methods to solve the PDE. However, since the source term is discontinuous at the boundary of a crystal the formal derivation of a finite difference method is not possible. Instead we use a finite element method to discretize space into a triangular mesh. The weak formulation of (4) is

$$\int_\Omega \frac{\partial T}{\partial t}\varphi_j(x) - \int_\Omega c^2 \nabla^2 T \varphi_j(x) = \int_\Omega D \frac{\partial I_\Theta}{\partial t}\varphi_j(x), \tag{5}$$

where Ω is the entire domain, and φ_j is a set of suitable test functions. We approximate the solution T by

$$T(x,t) \approx \sum_i u_i(t)\varphi_i(x). \tag{6}$$

We define

$$\begin{aligned} M_{ij} &= \textstyle\int_\Omega \varphi_i \varphi_j \\ A_{ij} &= \textstyle\int_\Omega c^2 \nabla \varphi_i \nabla \varphi_j \\ f_j &= \textstyle\int_\Omega D \frac{\partial I_\Omega}{\partial t} \varphi_j. \end{aligned} \tag{7}$$

By combining (5), (6), and (7) we arrive at the system of ODEs

$$M\dot{u} + Au = f \tag{8}$$

The matrices M and A are constant for all time. However the vector f is related to the latent heat liberated during the growth of a crystal and so is time dependent. In order to determine the value of f we use the pixel matrix used for the crystal growth.

The change in the pixel matrix gives an approximate value for the amount of latent heat liberated. This allows us to calculate the value of f. The resulting system of ODEs (8) can then be solved using a standard explicit method. For simplicity we use the Euler method.

4 Conclusions

The model of crystal growth was simulated for several different parameter values. The end results of two of the simulations are shown in figure 4. These simulations show that the faster the temperature of the polymer dropped the smaller the crystals that are formed. However, for practical purposes the rate of temperature decrease must not be too large otherwise the polymer will take on a glass like structure which has very different characteristics.

Due to time constraints, insufficient simulations were performed to determine the optimal cooling strategy for the polymer. However, if more time had been available the simulation of the model appears to be sufficiently robust as to provide qualitative information about the crystal growth within the polymer. It should be straight forward to generalise this simulation strategy to three dimensions, although the processing time and memory requirements will increase tremendously. Consequently it would be of benefit to look into other approaches of simulating this model for higher dimensions.

References

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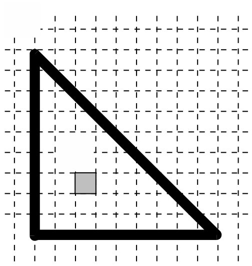
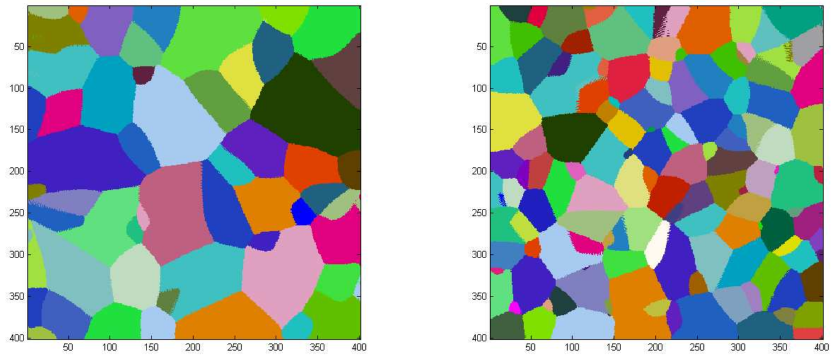


Figure 3: Single pixel in an element.



(a) (b)

Figure 4: Two simulations of crystal growth allowed to reach completion. The temperature decrease in panel (b) is faster than that of panel (a) leading to smaller crystals within the polymer.

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